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[54] **PITCH FOR CARBON FIBERS**

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[58] **Field of Search** 208/4, 22, 40, 6

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[57] **ABSTRACT**

A pitch which affords a carbon fiber having a high strength and a high elastic modulus is obtained by treating a pitch containing 5 to 35 wt. % of an optically anisotropic region with an oxidizing gas, followed by hydrogenation treatment if required.

3 Claims, No Drawings

PITCH FOR CARBON FIBERS

BACKGROUND OF THE INVENTION

The present invention relates to a modified pitch superior for use in the production of carbon fibers having a high strength and a high elastic modulus (Young's modulus).

At present, carbon fibers are prepared mainly from polyacrylonitrile. But the use of polyacrylonitrile is disadvantageous in that it is expensive, the original fibrous form easily gets out of shape at the time of heat carbonization treatment, and the carbonization yield is poor.

Recently, in view of such drawbacks, there have been reported a number of methods for producing carbon fibers from a less expensive pitch. However, carbon fibers obtained from pitch still involve a problem such that they are inferior in strength as compared with polyacrylonitrile carbon fibers.

It has recently been reported (see U.S. Pat. No. 4,005,183) that a carbon fiber superior in both elastic modulus and strength is obtainable by heat-treating a commercially available petroleum pitch to obtain a pitch containing 40 to 90 wt.% of an optically anisotropic liquid crystal called mesophase, the melt spinning the mesophase-containing pitch, rendering the resultant pitch fiber infusible, followed by carbonization and subsequent graphitization is required.

However, since a pitch containing not less than 40 wt.% of mesophase is extremely high in its softening point and viscosity, its melting spinning requires a high temperature usually not lower than 350° C. As a result, the pitch is apt to undergo a thermal decomposition in the course of melt spinning and produce a light gas, thus making it difficult to attain a uniform spinning.

In case the content of the mesophase is adjusted low with a view to adjusting the softening point and viscosity of the resulting pitch, there occurs separation between optically anisotropic and isotropic regions and the melt characteristic of the pitch is greatly deteriorated. More particularly, even if a pitch having a low mesophase content is subjected to melt spinning, there occurs breakage of thread frequently, and in the worst case the resultant fiber is like a linkage of unmelted particles, and even if such a fiber is treated by a conventional method, there is not obtained a carbon fiber having a high strength and a high elastic modulus.

SUMMARY OF THE INVENTION

It is an object of the present invention to eliminate the above-mentioned drawbacks of the prior art.

It is another object of the present invention to provide a process capable of improving the melt characteristic of a pitch of a low mesophase content having a low softening point and a low viscosity, thereby permitting a uniform spinning, and further capable of producing carbon fibers having a high strength and a high elastic modulus.

The above-mentioned objects of the present invention can be attained by treating a pitch having 5 to 35 wt.% of an optically anisotropic region with an oxidizing gas and preferably by subsequent hydrogenation treatment. By using the so-prepared pitch of the present invention, it is made possible to effect a uniform spinning and produce carbon fibers having a high strength and a high elastic modulus.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

A pitch containing 5 to 35 wt.% of mesophase is obtained by heat-treating a carbonaceous pitch such as a coal pitch or a petroleum pitch to allow mesophase to be formed.

The mesophase formation is carried out usually by heat treatment at a temperature ranging from 340° to 450° C., preferably 370° to 420° C., at atmospheric or reduced pressure. It is also preferable that this heat treatment be conducted while introducing an inert gas such as nitrogen gas. The duration of the heat treatment may vary according to conditions such as the treating temperature and the amount of inert gas introduced, but usually ranges from 1 minute to 30 hours, preferably 5 minutes to 20 hours. The amount of inert gas introduced is preferably in the range of 0.7 to 5.0 scfh/lb pitch.

The mesophase formation is carried out while adjusting to give a mesophase content of the pitch in the range of 5 to 35 wt.%. Outside this range, it is impossible to expect the effect of the present invention.

The pitch containing 5 to 35 wt.% of mesophase is then contacted with an oxidizing gas. Usually, the oxidizing gas is introduced into the pitch at a temperature ranging from 150° to 400° C., preferably 200° to 350° C., at atmospheric pressure or under application of pressure. The duration of this treatment may vary according to conditions such as the treating temperature and the amount of oxidizing gas introduced, but usually ranges from 5 minutes to 3 hours, preferably 10 minutes to 2 hours. The amount of oxidizing gas introduced is in the range of 0.5 to 5.0 scfh/lb pitch, preferably 1.0 to 3.5 scfh/lb pitch. This treatment should be controlled so that the softening point of the pitch may not become higher than 350° C. Such softening point is preferably not higher than 300° C. As the oxidizing gas, there may be used air, oxygen, ozone, nitrogen oxide, sulfurous acid gas, or a gaseous mixture of two or more thereof.

It is preferable that the contact treatment with the oxidizing gas be followed by hydrogenation treatment. As the hydrogenation treatment, there may be adopted a heterogeneous catalytic hydrogenation method using a solid catalyst, or a hydrogenation method using a hydrogen donating solvent such as tetralin. But, especially preferably, the hydrogenation treatment is carried out for usually 0.5 to 3 hours at a hydrogen pressure ranging from 30 to 300 kg/cm^2.G and at a temperature ranging from 300° to 500° C., preferably 350° to 450° C. The hydrogenation treatment in the present invention is carried out so that the mesophase content may not deviate from the range of 5 to 35 wt.%.

The pitch thus treated is then subjected to melt spinning by a conventional method.

The resultant pitch fiber is then rendered infusible in an oxidizing gas atmosphere. As the oxidizing gas, there may be used one or more of oxidizing gases such as oxygen, ozone, air, nitrogen oxide, halogen and sulfurous acid gas. This treatment for rendering the pitch fiber infusible is carried out under a temperature condition under which the melt-spun pitch fiber being treated does not soften and change in shape, for example, at a temperature in the range of 20° to 360° C., preferably 20° to 300° C. The duration of this treatment usually ranges from 5 minutes to 10 hours.

The pitch fiber thus rendered infusible is then subjected to carbonization and subsequent graphitization if required, in an inert gas atmosphere, to obtain carbon

fiber. The carbonization treatment is carried out at a temperature usually ranging from 800° to 2,500° C. Generally, the time required for carbonization is 0.5 minutes to 10 hours. Subsequently, graphitization may be performed, if required, at a temperature in the range of 2,500° to 3,500° C. for usually 1 second to 1 hour.

During the treatment for rendering the pitch fiber infusible or for carbonizing or graphitizing it, the pitch fiber being treated may be held under a slight load or tension.

The following examples and comparative examples are given to further illustrate the present invention, but it is to be understood that the invention is not limited thereto.

EXAMPLE 1

A heavy oil (properties of which are shown in Table 1) with a boiling point not lower than 200° C. by-produced in steam cracking of naphtha at 830° C. was heat-treated at 400° C. under a pressure of 15 kg/cm^2.G for 3 hours. The heat-treated oil thus obtained was distilled at 250° C./1 mmHg to distill off the light fraction therefrom to obtain a starting pitch (1) having a softening point of 82° C. 30 g. of the starting pitch (1) was heat-treated at 400° C. for 1 hour with stirring while nitrogen was introduced therein at a rate of 600 ml/min, to obtain a pitch (2) having a melting point of 220° C. and a mesophase content of 20 wt.%.

Then, 30 g. of the pitch (2) was stirred for 90 minutes at 300° C. while air was introduced therein at a rate of 600 ml/min, to obtain a pitch (3) having a softening point of 260° C. and a mesophase content of 20 wt.%.

The pitch (3) thus prepared was melt-spun at 330° C. by means of a spinning apparatus having a nozzle diameter of 0.3 mm and an L/D ratio of 2.0 to obtain pitch fiber of 16–19μ. The pitch fiber thus obtained was then rendered infusible, carbonized and graphitized under the following conditions to obtain carbon fiber.

Infusiblization Condition: Heat in an air atmosphere at a rate of 3° C./min up to 200° C. and 1° C./min up to 300° C., and hold at 300° C. for 30 minutes.

Carbonization Condition: Heat in a nitrogen atmosphere at a rate of 5° C./min and hold at 1,000° C. for 30 minutes.

Graphitization Condition: Heat in an argon gas stream up to 2,500° C. at a rate of 25° C./min.

The carbon fiber thus obtained proved to have a tensile strength of 160 kg/mm^2 and a Young's modulus of 30 ton/mm^2.

TABLE 1

Heavy oil properties		
Specific Gravity (15° C./4° C.)		1.039
Distillation Property	Initial boiling point	192° C.
	5%	200
	10%	206
	20%	217
	30%	227
	40%	241
	50%	263
	60%	290
	70%	360

COMPARATIVE EXAMPLE 1

The pitch (2) used in Example 1 was subjected, directly without going through the treatment with the oxidizing gas, to melt spinning in the same way as in Example 1. As a result, there occurred breakage of thread frequently and it was impossible to effect spinning continuously.

EXAMPLE 2

The starting pitch (1) used in Example 1 was heat-treated at 400° C. for 2 hours with stirring while nitrogen was introduced therein in the same way as in Example 1, to obtain a pitch (4) having a softening point of 230° C. and a mesophase content of 33 wt.%.

The pitch (4) was then stirred for 90 minutes at 300° C. while air was introduced therein in the same manner as in Example 1, to obtain a pitch (5) having a softening point of 270° C. and a mesophase content of 33 wt.%.

The pitch (5) thus obtained was melt-spun at 340° C. by means of the spinning apparatus used in Example 1 and then subjected to infusiblization, carbonization and graphitization treatments in the same way as in Example 1, to obtain carbon fiber.

The carbon fiber thus obtained proved to have a tensile strength of 190 kg/mm^2 and a Young's modulus of 35 ton/mm^2.

EXAMPLE 3

The starting pitch (1) used in Example 1 was heat-treated at 400° C. for 30 minutes with stirring while nitrogen was introduced therein in the same way as in Example 1, to obtain a pitch (6) having a softening point of 198° C. and a mesophase content of 8 wt.%.

The pitch (6) thus obtained was stirred for 90 minutes at 300° C. while air was introduced therein in the same manner as in Example 1, to obtain a pitch (7) having a softening point of 243° C. and a mesophase content of 8 wt.%.

The pitch (7) thus obtained was melt-spun at 315° C. by means of the spinning apparatus used in Example 1 and then subjected to infusiblization, carbonization and graphitization treatments in the same way as in Example 1 to obtain carbon fiber.

The carbon fiber thus obtained proved to have a tensile strength of 150 kg/mm^2 and a Young's modulus of 27 ton/mm^2.

EXAMPLE 4

A heavy oil (properties of which are shown in Table 2) obtained by subjecting a vacuum-distilled light oil from Arabic crude oil to catalytic cracking at 500° C. in the presence of a silica-alumina catalyst was heat-treated at 430° C. under a pressure of 15 kg/cm^2.G for 3 hours. The heat-treated oil thus obtained was distilled at 250° C./1 mmHg to distill off the light fraction therefrom to obtain a starting pitch (8) having a softening point of 85° C. 30 g. of the starting pitch (8) was heat-treated at 400° C. for 1.5 hours while nitrogen was introduced therein in the same way as in Example 1, to obtain a pitch (9) having a softening point of 225° C. and a mesophase content of 32 wt.%.

The pitch (9) thus obtained was then stirred for 90 minutes at 300° C. while air was introduced therein in the same manner as in Example 1, to obtain a pitch (10) having a softening point of 260° C. and a mesophase content of 32 wt.%.

The pitch (10) thus obtained was melt-spun at 330° C. by means of the apparatus used in Example 1 and then subjected to infusiblization, carbonization and graphitization treatments in the same way as in Example 1 to obtain carbon fiber.

The carbon fiber thus obtained proved to have a tensile strength of 225 kg/mm^2 and a Young's modulus of 43 ton/mm^2.

TABLE 2

Heavy oil properties		
Specific Gravity (15° C./4° C.)		0.965
Distillation Property	Initial boiling point	320° C.
	5%	340
	10	353
	20	370
	30	385
	40	399
	50	415
	60	427
	70	445
	80	467
	90	512
Viscosity cSt @ 50° C.		18.21

EXAMPLE 5

50 g. of the pitch (3) obtained in Example 1 was charged into a 300 ml. autoclave and subjected to hydrogenation treatment for 1 hour with stirring at a hydrogen pressure of 150 kg/cm^2.G and at a temperature of 360° C. to obtain a pitch (11) having a softening point of 245° C. and a mesophase content of 20 wt.%.

The pitch (11) thus prepared was melt-spun at 315° C. by means of a spinning apparatus used in Example 1 to obtain pitch fiber of 14–17μ, and then subjected to infusiblization, carbonization and graphitization treatments in the same way as in Example 1, to obtain carbon fiber.

The carbon fiber thus obtained proved to have a tensile strength of 200 kg/mm^2 and a Young's modulus of 32 ton/mm^2.

COMPARATIVE EXAMPLE 2

In the same way as in Example 5, the pitch (2) used in Example 1 was hydrogenated for 1 hour with stirring at a hydrogen pressure of 150 kg/cm^2.G and at a temperature of 360° C. to obtain a pitch (12) having a softening point of 250° C. and a mesophase content of 35 wt.%.

The pitch (12) thus obtained was melt-spun at 320° C. by means of the spinning apparatus used in Example 1. But, due to a frequent breakage of thread it was impossible to effect spinning continuously.

EXAMPLE 6

In the same way as in Example 5, the pitch (4) obtained in Example 2 was subjected to hydrogenation treatment for 1 hour with stirring at a hydrogen pressure of 150 kg/cm^2.G and at a temperature of 360° C., to obtain a pitch (13) having a softening point of 255° C. and a mesophase content of 33 wt.%.

The pitch (13) thus obtained was melt-spun at 330° C. by means of the spinning apparatus used in Example 1 and then subjected to infusiblization, carbonization and graphitization treatments in the same manner as in Example 1, to obtain carbon fiber.

The carbon fiber thus obtained proved to have a tensile strength of 230 kg/mm^2 and a Young's modulus of 40 ton/mm^2.

EXAMPLE 7

In the same way as in Example 5, the pitch (7) obtained in Example 3 was subjected to hydrogenation treatment for 1 hour with stirring at a hydrogen pressure of 150 kg/cm^2.G and at a temperature of 360° C., to obtain a pitch (14) having a softening point of 230° C. and a mesophase content of 8 wt.%.

The pitch (14) thus obtained was melt-spun at 300° C. by means of the spinning apparatus used in Example 1 and then subjected to infusiblization, carbonization and graphitization treatments in the same manner as in Example 1, to obtain carbon fiber.

The carbon fiber thus obtained proved to have a tensile strength of 180 kg/mm^2 and a Young's modulus of 30 ton/mm^2.

EXAMPLE 8

In the same way as in Example 5, the pitch (10) used in Example 4 was subjected to hydrogenation treatment for 1 hour with stirring at a hydrogen pressure of 150 kg/cm^2.G and at a temperature of 360° C., to obtain a pitch (15) having a softening point of 250° C. and a mesophase content of 32 wt.%.

The pitch (15) thus obtained was melt-spun at 320° C. by means of the spinning apparatus used in Example 1 and then subjected to infusiblization, carbonization and graphitization treatments in the same way as in Example 1, to obtain carbon fiber.

The carbon fiber thus obtained proved to have a tensile strength of 270 kg/mm^2 and a Young's modulus of 50 ton/mm^2.

What is claimed is:

1. In the production of carbon fibers, a process for preparing a pitch used therein comprising, heat treating a carbonaceous pitch to form a content of 5 to 35 weight percent of an optically anisotropic region and oxidizing said treated pitch with air, oxygen, ozone, nitrogen oxide, sulfurous gas or mixtures thereof, the oxidizing gas being introduced at a temperature of about 150° C. to about 400° C. and at a pressure of about 0.5 to about 5.0 scfh/lb. of pitch for about 5 minutes to about 3 hours.

2. The process of claim **1** which further comprises hydrogenating the oxidized pitch from about 0.5 to about 3 hours while maintaining said optically anisotropic content of said pitch during said hydrogenation, said hydrogenation being carried out at a hydrogen pressure of about 30 to about 300 kg/cm^2.G and at a temperature from about 300° C. to about 500° C.

3. The process of claim **1** which further comprises introducing an inert gas during heat treatment of the pitch.

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